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<b>(21) International Application Number:</b> PCT/US97/13780 <b>(22) International Filing Date:</b> 6 August 1997 (06.08.97) <b>(30) Priority Data:</b> 08/693,657 9 August 1996 (09.08.96) US <b>(71) Applicant (for all designated States except US):</b> MTC LTD. [IL/IL]; P.O. Box 4504, 91044 Jerusalem (IL). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> GABBAY, Jeffrey [US/IL]; Jabotinsky 14/21, 92142 Jerusalem (IL). <b>(74) Agent:</b> FRIEDMAN, Mark, M.; c/o Sheinbein, Robert, 2940 Birchtree Lane, Silver Spring, MD 20906 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> APPLICATIONS OF METALLIZED TEXTILE  <b>(57) Abstract</b>  Applications of a metallized textile. The textile is activated by precipitating noble metal nucleation sites on the fibers of the textile. Immersing the activated textile in a suitable prepared solution of a metal cation, and adding a reducing agent, leads to the formation of a metal plating tightly and intimately bonded to the fibers of the textile. Exposure of the metallized textile to air oxidizes the surface of the metal plating. Applications of the metallized textile include acaricides, fungicides, bactericides, armor, electrodes, anti-static devices, RF shielding, and radar reflectors.		

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## APPLICATIONS OF METALLIZED TEXTILE

### FIELD AND BACKGROUND OF THE INVENTION

5       The present invention relates to textiles and, more particularly, to applications of a metallized textile produced by binding a full or partial metal or metal oxide plating to the fibers of a textile.

There are a variety of applications for which a textile with a full or partial metal or metal oxide plating bonded to the fibers thereof would be  
10 useful. These include:

1.     Acaricide

Beds commonly are infested by tiny mites. These mites eat bacteria and fungi that grow on epidermal scales shed by people who sleep in the beds. Fragments of dead mites, and mite excreta, are allergens, to which  
15 asthmatics and people with dust allergens are sensitive. It has been found that some metals and metal oxides, notably Cu, CuO, Ag and Ag<sub>2</sub>O, repel mites.

The conventional method for making textiles inhospitable to mites is to treat the textiles with an organic acaricide such as benzyl benzoate.  
20 For example, Bischoff et al., in U.S. Patent No. 4,666,940, teach an acaricide that includes benzyl benzoate and a solid powder carrier whose particles are of a size suitable for ingestion by the mites. These acaricides

must be replaced every time the textile is laundered. Thus, Bischoff et al. recommend using their acaricide on textiles, such as carpets and upholstery, that are not laundered frequently. An inherently acaricidal bedsheet would keep a bed free of mites, even after multiple launderings, without the need to reapply acaricide to the bedsheet.

## 2. Bactericide and Fungicide

Some metal oxides, notably ZnO, are well known as fungicides. Before the introduction of antibiotics to medicine, silver metal sometimes was used as a bactericide and bacteriostat. Textiles with inherent bactericidal and fungicidal properties have obvious applications in settings, such as hospitals and similar institutions, where it is important to maintain aseptic conditions.

Bactericidal agents used heretofore in textiles include complexes of zirconyl acetate with inorganic peroxides (Welch et al., U.S. Patent No. 4,115,422), metal cations contained in zeolite particles (Hagiwara et al., U.S. Patent No. 4,525,410), and quaternary ammonium salts (White et al., U.S. Patent No. 4,835,019; Hill et al., U.S. Patent No. 5,024,875; Zhao et al., U.S. Patent No. 5,254,134). These are not totally satisfactory, being specific to a particular textile (such as the polyamide yarn of White et al.), or being subject to eventual loss of activity by chemical decomposition, a process often hastened by laundering.

### 3. Body Armor

Lightweight armor commonly is made of multiple layers of fibers such as the fiber produced by E. I. DuPont de Nemours and Company under the trademark Kevlar. It has been found that the effectiveness of Kevlar armor is enhanced by the inclusion of ceramics such as  $\text{Al}_2\text{O}_3$ , in the form of plates, or, as taught by Clausen in U.S. Patent No. 4,292,882, in the form of particles interspersed among the Kevlar fibers. These ceramics enhance the resistance of the armor to penetration by bullets, by abrading and gripping the bullets. This action would be enhanced further in armor in which the  $\text{Al}_2\text{O}_3$  has an even more intimate connection to the Kevlar fibers.

The methods known in the prior art for bonding a metal or a metal oxide to a textile generally require that the metal or its oxide be bonded indirectly to the textile. For example, the metal may be reduced to a powder and suspended in a binder. The binder-metal mixture then is applied to the textile, with the binder, and not the metal, bonding to the textile. Alternatively, the metal is reduced to a powder, an adhesive is applied to the textile, and the metal powder is spread on the adhesive. Examples of both such methods may be found in U.S. Patent No. 1,210,375, assigned to Decker. These methods are less than satisfactory for the above applications, for at least two reasons. First, the carrier or adhesive may entirely encapsulate the metal or metal oxide powder

particles, inhibiting their contact with mites, fungi, and bacteria, and making the textile useless as an acaricide, fungicide, or bactericide.

Second, multiple launderings tends to weaken the binder or adhesive and loosen or remove the particles.

5 Two notable exceptions to the general rule that metals and metal oxides have not heretofore been bonded directly to textiles are nylon textiles and polyester textiles, which may be plated with metals using standard electroless plating processes for plating plastics. The specific electroless plating methods known to the art are restricted in their applicability to only certain plastics, however. In particular, they are not  
10 suited to natural fibers, nor to most synthetic fibers.

There is thus a widely recognized need for, and it would be highly advantageous to have, a textile with a full or partial metal or metal oxide plating directly and securely bonded to the fibers thereof, for use in the  
15 applications listed above. The scope of the present invention includes these and other applications, which are listed below.

### SUMMARY OF THE INVENTION

According to the present invention there is provided a process comprising the steps of: (a) providing a metallized textile, the metallized  
20 textile comprising: (i) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated

fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and (ii) a plating including materials selected from the group consisting of metals and metal oxides, the metallized textile characterized in that the plating is bonded directly to the fibers; and (b) 5 incorporating the metallized textile in an article of manufacture.

In the context of the present invention the term "textile" includes fibers, whether natural (for example, cotton, silk, wool, and linen) or synthetic, yarns spun from those fibers, and woven, knit, and non-woven fabrics made of those yarns. The scope of the present invention includes 10 all natural fibers; and all synthetic fibers used in textile applications, including but not limited to synthetic cellulosic fibers (i.e., regenerated cellulose fibers such as rayon, and cellulose derivative fibers such as acetate fibers), regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, and vinyl fibers, but excluding nylon and polyester 15 fibers; and blends thereof.

The present invention comprises applications of the products of an adaptation of technology used in the electroless plating of plastics, particularly printed circuit boards made of plastic, with metals. See, for example, Encyclopedia of Polymer Science and Engineering (Jacqueline 20 I. Kroschwitz, editor), Wiley and Sons, 1987, vol. IX, pp 580 - 598. As applied to textiles, this process includes two steps. The first step is the activation of the textile by precipitating catalytic noble metal nucleation

sites on the textile. This is done by first soaking the textile in a solution of a low-oxidation-state reductant cation, and then soaking the textile in a solution of noble metal cations, preferably a solution of  $\text{Pd}^{++}$  cations, most preferably an acidic  $\text{PdCl}_2$  solution. The low-oxidation-state cation  
5 reduces the noble metal cations to the noble metals themselves, while being oxidized to a higher oxidation state. Preferably, the reductant cation is one that is soluble in both the initial low oxidation state and the final high oxidation state, for example  $\text{Sn}^{++}$ , which is oxidized to  $\text{Sn}^{++++}$ , or  $\text{Ti}^{+++}$ , which is oxidized to  $\text{Ti}^{++++}$ .

10 The second step is the reduction, in close proximity to the activated textile, of a metal cation whose reduction is catalyzed by a noble metal. Examples of such cations include  $\text{Cu}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{++}$  and  $\text{Ni}^{++}$ . The reducing agents used to reduce the cations typically are molecular species, for example, formaldehyde in the case of  $\text{Cu}^{++}$ , and hydrazine hydrate in  
15 the case of  $\text{Ag}^{+++}$ . Because the reducing agents are oxidized, the metal cations are termed "oxidant cations" herein. After these oxidant cations are plated on the textile, the metal plating may be processed further, for example, by oxidation to the oxide. This oxidation is most conveniently effected simply by exposing the metallized textile to air. The metallized  
20 textiles and the oxide-plated textiles thus produced are characterized in that their metal or metal oxide plating is bonded directly to the textile fibers.



The plating may cover substantially all of the fiber surfaces, or may cover only part of the surfaces.

As bactericides and fungicides, the metallized textiles thus produced have a variety of applications. They may be used to make garments, such as socks, which inhibit infections such as athlete's foot and jock itch. They may be used to make intrinsically antiseptic bandages. They may be used in interior furnishings, such as floor coverings including carpets, wall coverings, curtains, and upholstered furniture: in hospitals, where they inhibit the spread of nosocomial infections, and as interior furnishings generally in warm, humid climates to inhibit mildew. They may be incorporated in food storage containers to lengthen the shelf life of the food stored therein.

Because the metallized textiles thus produced conduct electricity, they have a variety of electrical applications that exploit their flexibility and relatively light weight compared to fabrics woven from pure metals. They may be used as electrodes in applications, such as medical applications, in which flexibility, to match the contours of a patient's body, is an advantage. Similarly, they may be used as electrodes in lightweight batteries. They may be used as anti-static devices: for example, in carpets, to prevent static buildup in rooms where electronic devices sensitive to static, such as computers, are used; or in automotive upholstery, as taught by Hatamoto et al. in U.S. Patent No. 5,009,946.

They may be used as radio frequency shields to prevent eavesdropping on cordless telephone conversations or on stray electronic signals generally. In this application, they are aesthetically more pleasing than the metallic screens conventionally used for this purpose. They may be used in radar-  
5 reflective camouflage nets.

Finally, the textiles thus produced may be used as fire retardants, for example in fire barriers, garments, and public transportation vehicles.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of applications of metallized textiles  
10 produced by binding a full or partial metallic plating to a textile. Specifically, the various applications that comprise the present invention employ textiles with metal and metal oxide coatings intimately and permanently bonded to the fibers of those textiles.

The process of plating a textile with a metal or metal oxide for use  
15 in the applications of the present invention may be better understood with reference to the following Examples. These Examples are illustrative, and should not be construed to restrict the scope of the present invention in any way.

#### EXAMPLE 1

20 A dilute acidic solution of  $\text{SnCl}_2$  was prepared by dissolving  $\text{SnCl}_2$  and concentrated  $\text{HCl}$  in water.

An dilute acidic solution of  $\text{PdCl}_2$  was prepared by dissolving  $\text{PdCl}_2$  and concentrated  $\text{HCl}$ , and water.

An 8" x 3" cotton swatch was activated as follows:

Soak in a bath of the  $\text{SnCl}_2$  solution.

5        Soak in a bath of the  $\text{PdCl}_2$  solution.

A dilute basic  $\text{CuSO}_4$  solution was prepared by dissolving  $\text{CuSO}_4$  and  $\text{NaOH}$  (in approximately equal weight proportions), a chelating agent, and polyethylene glycol in water.

The activated cotton swatch and formaldehyde were added to the  
10  $\text{CuSO}_4$  solution under a pure oxygen atmosphere. After between 2 minutes and 10 minutes, the cotton swatch was removed.

The palladium deposited on the cotton swatch in the activation step catalyzed the reduction of the  $\text{Cu}^{++}$  by the formaldehyde, providing a layer of copper tightly and intimately bonded to the fibers of the cotton  
15 swatch. The swatch, which initially was white in color, now was the color of copper metal, while retaining the flexibility and physical characteristics of the original fabric. The metallic copper color remained unchanged after several launderings.

## EXAMPLE 2

20        An 8" x 3" cotton swatch was activated as in Example 1. A dilute solution of  $\text{AgNO}_3$  was prepared by dissolving  $\text{AgNO}_3$ , concentrated

$\text{NH}_4\text{OH}$ , and glacial acetic acid in water. The volume ratio of concentrated  $\text{NH}_4\text{OH}$  to glacial acetic acid was about 1.7 to 1.

The activated cotton swatch, and dilute aqueous hydrazine hydrate, were added to the  $\text{AgNO}_3$  solution. After 10 minutes, the cotton swatch 5 was removed.

The palladium deposited on the cotton swatch in the activation step catalyzed the reduction of the  $\text{Ag}^+$  by the hydrazine hydrate, providing a partially oxidized layer of silver tightly and intimately bonded to the fibers of the cotton swatch. The swatch, which initially was white in color, now 10 was dark gray. The dark gray color remained unchanged after several launderings.

While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

## WHAT IS CLAIMED IS:

1. A process comprising the steps of:
  - (a) providing a metallized textile, said metallized textile comprising:
    - (i) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and
    - (ii) a plating including materials selected from the group consisting of metals and metal oxides,said metallized textile characterized in that said plating is bonded directly to said fibers; and
  - (b) incorporating said metallized textile in an article of manufacture.
2. The process of claim 1, wherein said article of manufacture is an acaricide.
3. The process of claim 2, wherein said article of manufacture is a bedsheet.

4. The process of claim 1, wherein said article of manufacture is a fungicide.

5. The process of claim 4, wherein said article of manufacture is a garment.

6. The process of claim 4, wherein said article of manufacture is a food storage container.

7. The process of claim 1, wherein said article of manufacture is a bactericide.

8. The process of claim 7, wherein said article of manufacture is a garment.

9. The process of claim 7, wherein said article of manufacture is a bandage.

10. The process of claim 7, wherein said article of manufacture is an interior furnishing.

11. The process of claim 10, wherein said article of manufacture is a floor covering.

12. The process of claim 11, wherein said article of manufacture is a carpet.

13. The process of claim 10, wherein said article of manufacture is a wall covering.

14. The process of claim 10, wherein said article of manufacture is an article of furniture.

15. The process of claim 10, wherein said article of manufacture is a curtain.

16. The process of claim 7, wherein said article of manufacture is a food storage container.

17. The process of claim 1, wherein said article of manufacture is armor.

18. The process of claim 17, wherein said article of manufacture is body armor.

19. The process of claim 1, wherein said article of manufacture is an electrical device.

20. The process of claim 19, wherein said article of manufacture is a battery.

21. The process of claim 1, wherein said article of manufacture is an electrode.

22. The process of claim 1, wherein said article of manufacture is an anti-static device.

23. The process of claim 22, wherein said article of manufacture is a carpet.

24. The process of claim 22, wherein said article of manufacture is upholstery.



25. The process of claim 1, wherein said article of manufacture is a radio frequency shield.

26. The process of claim 1, wherein said article of manufacture is a radar reflector.

27. The process of claim 1, wherein said article of manufacture is a fire retardant.

28. The process of claim 1, wherein said article of manufacture is a fire barrier.

29. The process of claim 1, wherein said article of manufacture is a garment.

30. The process of claim 1, wherein said article of manufacture is a vehicle.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/13780

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B05D 3/04, 3/10

US CL : 427/304

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/304, 383.1; 428/379, 389; 442/231, 317, 379

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,900,618, A, (O'CONNER et al) 13, February 1990, col 2, line 41-61, col. 5, lines 17-27 and col. 6, lines 8-12.	1, 19, 21-22, 25-26 ----- 2-18, 20, 23-24, 27-30
A	US 4, 999,240 A (BROTZ) 12 March 1991, all	1-30
X --- Y	US 5,017,420 A (MARIKAR et al) 21 May 1991, abstract, col. 4, lines 55-60, col. 18, lines 3-15 and col. 19, lines 5-10.	1, 19, 21-26, 29 ----- 2-18, 20, 27, 30
X	US 5,399,425 A (BURCH) 21 March 1995, abstract and col. 1, lines 12-20.	1, 19-22, 25-26

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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JILL M. GRAY

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,405,644 A (OHSUMI et al) 11 April 1995, abstract, col. 1, lines 5-20, col. 2, lines 30-62 and col. 8, lines 40-44.	1, 4-5, 7-10, 17-18 ----- 2-3, 6, 11-16
X	US 5,411,795 A (SILVERMAN) 02 May 1995, col. 2, lines 38-43, col. 3, lines 63-68 and col. 5, lines 29-54.	1, 19, 21-22, 29 ----- 2-18, 20, 23-28, 30